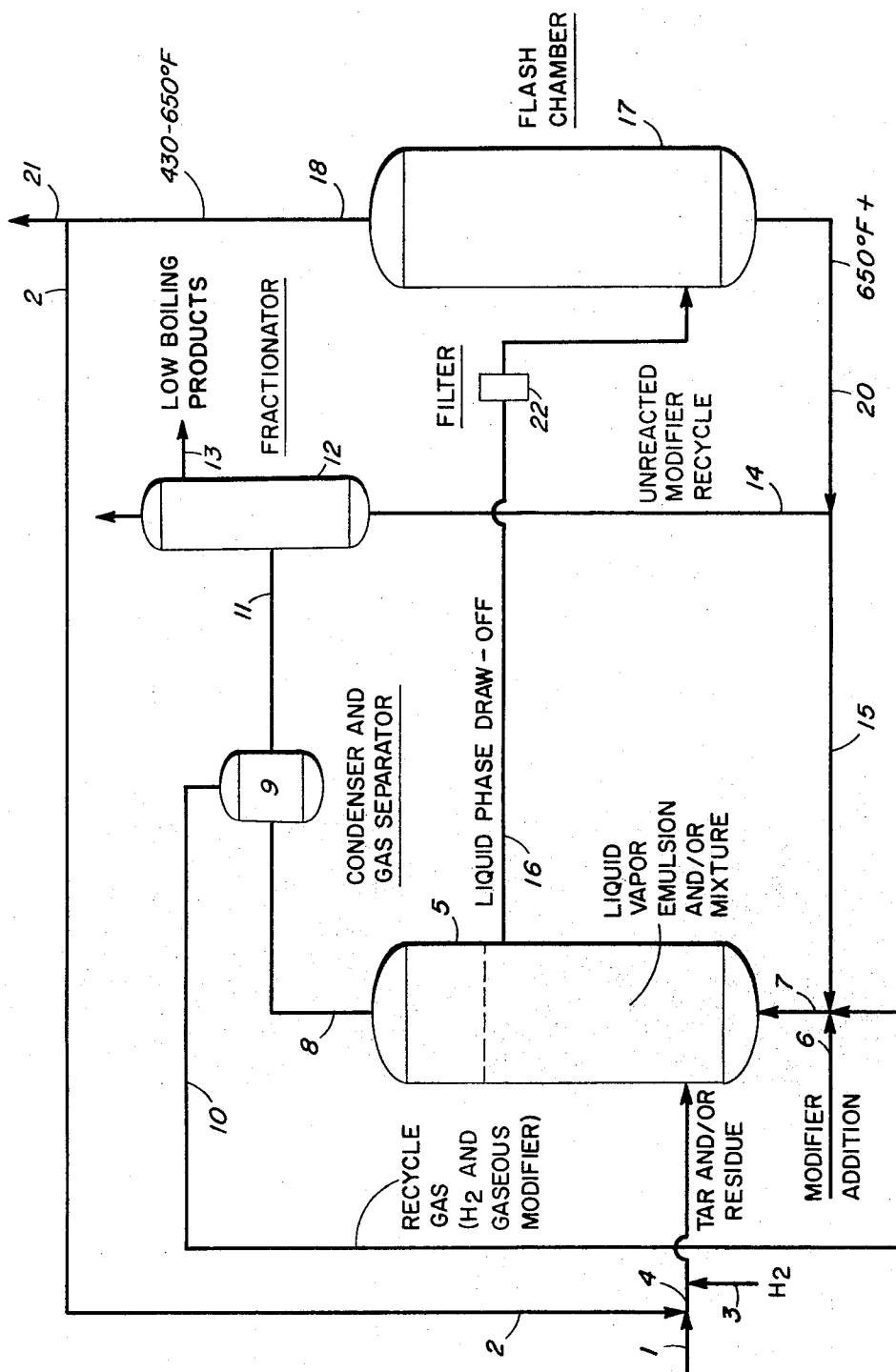


CRACKING HYDROCARBON RESIDUA

Filed April 17, 1970

2 Sheets-Sheet 1

FIGURE 1



Dec. 26, 1972

R. B. MASON ETAL

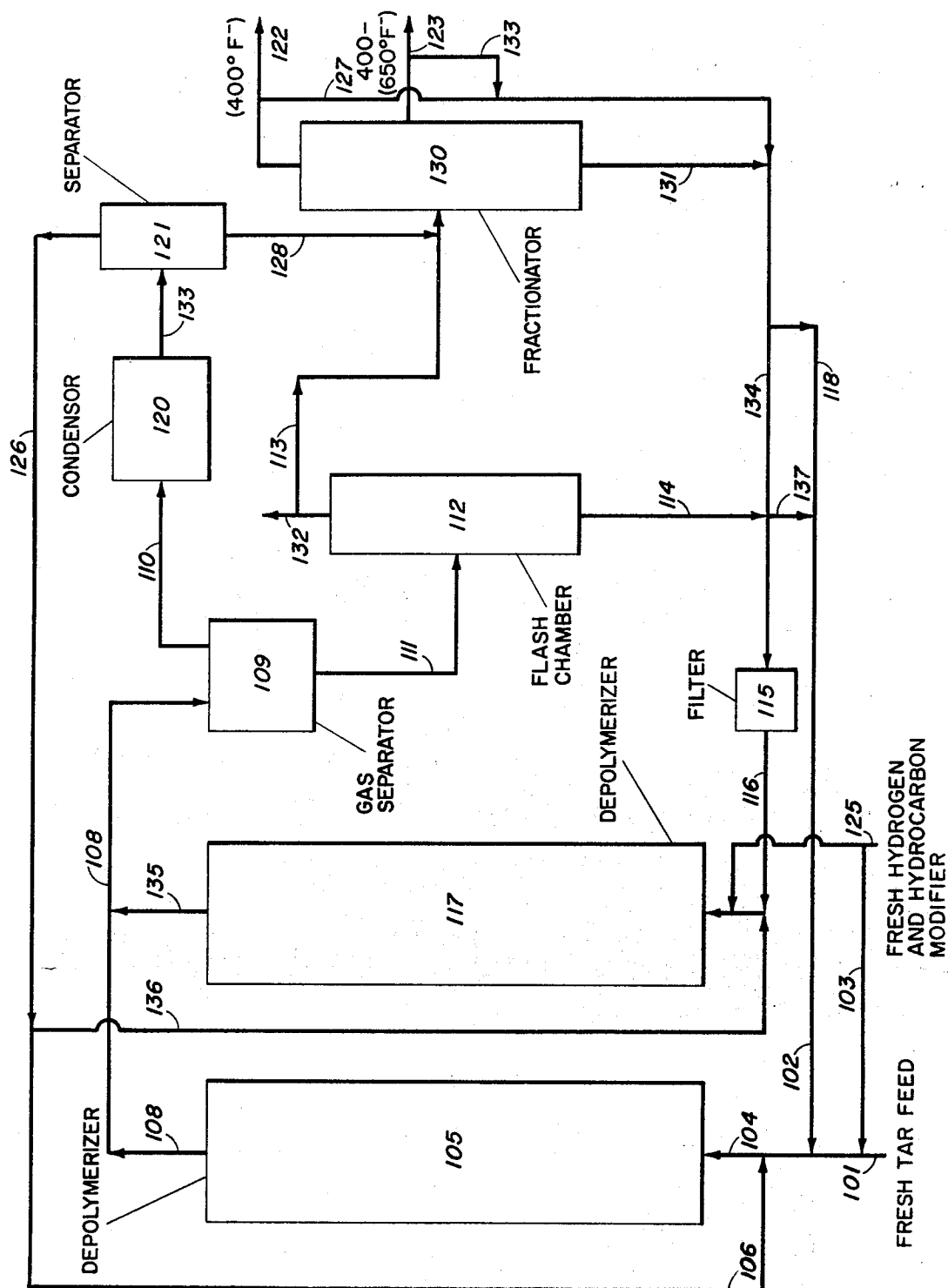
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CRACKING HYDROCARBON RESIDUA

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Figure 2



1

3,707,459

CRACKING HYDROCARBON RESIDUA

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Continuation-in-part of abandoned application Ser. No. 839,220, July 7, 1969. This application Apr. 17, 1970, Ser. No. 29,629

Int. Cl. C10g 9/00, 13/00, 37/02

U.S. Cl. 208—76

26 Claims

ABSTRACT OF THE DISCLOSURE

Hydrocarbon residua boiling mostly 1000° F. and above are depolymerized in the presence or absence of hydrogen in one or more stages under liquid phase conditions to obtain a product which is predominantly an aromatic gas oil and eminently suitable either as a solvent or as feed to hydrocracking operations. Although the upper boiling limit of this gas oil may be in the range of 600 to 1000° F., the process is illustrated by two schemes, one in which the gas oil is separated into fractions boiling 430–650° F., 650–1000° F. and 1000° F.+ and the other in which the gas oil is separated into 430–650° F. and 650° F.+ fractions. In each scheme an amount of the low-boiling fraction is recycled so that the feed mixture to the reaction zone contains 20 to 50% of the low-boiling fraction while the high boiling fraction is recycled at a rate such that the amount present in the feed mixture to the reactor is equal to the amount in the make product thus resulting in balanced conditions. 1–25% of an acyclic hydrocarbon modifier and/or a mild alkali is added to the reaction mixture to act as a free-radical acceptor. When a hydrocarbon is used it has a residence time of one hour or less as compared to 1 to 6 hours for the residua-recycle mixture.

RELATED APPLICATIONS

This is a continuation-in-part of application Ser. No. 839,220 filed July 7, 1969 now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the thermal conversion of hydrocarbon residua and more particularly relates to the visbreaking of heavy residua under conditions of extinction recycle.

It is expected that steam cracking facilities will expand in the future, particularly in Europe. This will require means for easily disposing of the considerable amounts of tar which are a concomitant part of the steam-cracking process. One obvious method is to upgrade these tars as well other residues by thermally-treating the tars with a hydrogen donor diluent material. The donor diluent is a hydrogen containing material, aromatic-naphthenic in nature, that has ability to take up hydrogen in a hydrogenation zone and readily release it to a hydrogen-deficient oil in a thermal cracking zone. Unfortunately, however, there is often undesired coke deposition at hot spots and preheater zones, leading to plugging of the equipment.

SUMMARY OF THE INVENTION

In accordance with this invention the above disadvantages are overcome by subjecting hydrocarbon residues boiling mostly 1000° F. and above to thermal depolymerization or visbreaking in the liquid phase in the presence or absence of hydrogen and in the presence of a free radical acceptor, such as an acyclic hydrocarbon and/or a mild alkali. One or more stages may be used. In the case of single stage operation a high-boiling material is recycled

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to extinction and a low-boiling material is recycled so that the amount recycled plus that in the feed is maintained between 20 and 50% and preferably at about 30% of the total composition fed to the reaction zone. The amount of high-boiling material in the recycle and the amount in the product are kept at about the same level, generally leveling off at about 47% so as to maintain balanced conditions. The low boiling material has a boiling range beginning well below 650° F., e.g. 430° F. and ending at least as high as 650° F. and even as high as 1000° F.

When multistage operation is used the initial stage or stages are carried out under mild conditions, after which 45–50% of the high-boiling product from the initial stage or stages is blended with 20–50% of the low-boiling product, based on total blend, and depolymerized in one or more additional stages under somewhat more severe conditions. Conversion of the high-boiling fraction from the first stage or stages is maintained between 25–40% and in the succeeding stage or stages 25–30%.

In this embodiment it is not necessary to operate under balanced conditions in the initial stage. If balanced conditions are maintained the high-boiling fraction is recycled to extinction and divided between the stages such that the total recycle from all the stages is equal to the amount in the feed to the first reactor.

Yields of 95 vol. percent of the low-boiling product can be obtained with small losses to gas and coke. The multistage process yields even smaller losses.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 represents in diagrammatic form a method for carrying out the invention using a single stage.

FIG. 2 represents in diagrammatic form a method for carrying out the invention in two stages.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to FIG. 1, a hydrocarbon residue having a Conradson carbon number between 5 and 40 and a substantial amount boiling at 1000° F. and above, such as thermal tar from steam cracking, reduced crude, shale oil residue, liquefied coal fractions, and the like is fed by line 1 and mixed with lower boiling material, such as gas oil, preferably recycled from a later stage of the process which enters through line 2, mixed with 50–5000 s.c.f. of hydrogen or a nonoxidizing gas per barrel of feed from line 3. Gas oil or the like acts as a solvent for the tar and permits easy pumping at moderate temperatures and prevents coking at hot spots in the system. In case the feed material has been stored for sometime or has otherwise had a chance to pick up small amounts of oxygen, it may be desirable to subject it to a preliminary deoxygenation step in which it is contacted with a suitable deoxygenation catalyst, such as reduced copper, nickel or cobalt at a temperature below 700° F., preferably between 430 and 650° F. The feed mixture is passed by line 4 into the bottom of depolymerizer or visbreaker 5 where the mixture is maintained at a temperature of 700–900° F. (preferably 750–770° F.) and under sufficient pressure to maintain it in the liquid phase, e.g. 50–1000 p.s.i.g. A free-radical acceptor or modifier, preferably an acyclic hydrocarbon, which may be a paraffin or iso-paraffin of 4 to 20 carbon atoms per molecule, or an olefin or iso-olefin of 2 to 20 carbon atoms per molecule or mixtures thereof is added by lines 6 and 7. Suitably hydrocarbons include the paraffins n-heptane and n-pentane, 2,2,4-trimethyl pentane, the olefins, 2,4,4-trimethyl pentene-1, and 2,4,4-trimethyl pentene-2, as well as other olefins of similar skeletal configurations, low octane unsaturated naphtha fractions, normal C₅–C₇ virgin naphtha, catalytic heavy naphtha, heavy alkylates, a

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100–165° F. hydroformate fraction and the 210–400° F. fraction made by polymerizing propylenes and butylenes with H_3PO_4 on kieselguhr [Hydrocarbon Processing, V. 47: 170 (September 1968)], and the like. These hydrocarbons are added in amounts of about 1 to 25% based on tar feed and are sprayed, jetted or otherwise passed through the liquid tar phase in depolymerizer 5, into the vapor phase and removed overhead through line 8. The residence time of the modifier added through line 7 should range from about 5 minutes to one hour. The presence of the hydrocarbon modifiers at such short residence times results in reduced coke and gas loss. However, some of the modifier is consumed in the process. When n-heptane is the modifier the degradation products are predominantly normal hydrocarbons, namely, n-butane, n-pentane, n-hexane, etc. whereas when iso-octane is used the degradation products are predominantly branched, i.e., isobutane, isopentane and branched C_6 and C_7 paraffins. The use of 2,2,4-trimethyl pentane and olefins of a similar skeletal configuration results in the production of the important blending agent, triptane. Without intending to limit the invention to any theory of what occurs, it is believed that the mechanism is one in which the modifier is being consumed with accompanying hydrogen exchange, demethanation, alkylation, isomerization, aromatic disproportionation and probably every known hydrocarbon reaction. The most plausible explanation is a free-radical mechanism in which the condensed ring aromatic components of the tar depolymerize with the formation of free-radicals which attach themselves to the modifier as a "sink". In doing so the modifier in turn forms free radicals involving stepwise degradation and rearrangement reactions leading to gaseous products, coke, etc.

From the above it appears that conditions of short residence times for the modifier (less than one hour) coupled with fairly long residence times for the tar feed (one to six hours) is important for best results.

If desired a solid free radical acceptor may be slurried with the feed introduced through line 1. The alkaline material may be any mild alkali such as Na_2CO_3 , CaO , $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, Li_2CO_3 , CaCO_3 , BaCO_3 , MgCO_3 , $\text{Mg}(\text{OH})_2$ sodalite or the like. When the alkali is added along with the hydrocarbon modifier, it is used in amounts of 0.1 to 1 part by weight of alkali per part by weight of feed. However, if desired, the alkali may be used alone in which case it is added in amounts of 0.1 to 50 weight percent based on feed.

The hydrocarbon modifier leaving depolymerizer 5 through line 8 is passed to separator 9 from which hydrogen and uncondensed gas is recycled by line 10. Condensate from separator 9 is passed by line 11 to fractionator 12 from which low boiling products are removed by line 13 and unreacted modifier and entrained higher boiling components by line 14. This unreacted modifier is recycled to depolymerizer 5 by lines 15 and 7.

Liquid products are withdrawn from depolymerizer 5 by line 16 and passed through filter 22 where coke and/or other solid contaminants are removed and then passed to flash chamber 17 where they are separated into high and low-boiling products. The cut point between the low-boiling and high-boiling products may vary between 650° F. and 1000° F. In one example, those boiling below 650° F. are either drawn off as make products through lines 18 and 21 or are recycled to depolymerizer by lines 18, 2 and 4. Products boiling above 650° F. are recycled by lines 20, 15 and 7. In another example, the low-boiling products recycled through lines 18 and 21 or 18, 2 and 4 boil 1000° F. The high-boiling materials boil above 1000° F.

The amount of low-boiling products recycled by lines 18, 2 and 4 is critical, and must be between 20 and 50% of the total composition regardless of the distribution of the other materials. This control is made possible by withdrawing an amount of high-boiling material from the sys-

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tem by line 21 necessary to maintain the proper recycle ratio. The product drawn off through line 21 is suitable as such, as solvent for use in the chemical industry or may be further fractionated to separate out desired solvent and aromatic fractions and if desired with recycle of the high-boiling material.

The recycle of the high-boiling material on the other hand is controlled so that the amount of this material fed to the depolymerizer based on total feed will be substantially the same as the amount of this high-boiling material found in the product, based on tar blend. Generally this is between 45 and 50%, preferably 46–47%. While it is not intended to be bound by any theory as to the mechanism involved, it is believed that the beneficial results obtained are due to an equilibrium phenomenon in which an equilibrium exists between the condensed ring aromatic-containing high-boiling fraction and the lower boiling depolymerized fraction. Excessive amounts of the low-boiling fraction will retard the depolymerization, limit throughput of the depolymerization feed and incur excessive handling costs.

Referring now to FIG. 2, a hydrocarbon residue having a Conradson carbon number between 5 and 40 and a substantial amount boiling 1000° F. and above, such as thermal tar from steam cracking, reduced crude, shale oil residue, liquified coal fractions, and the like is fed by line 101 and mixed with lower boiling material, such as gas oil, preferably recycled from a later stage of the process which enters through line 102, mixed with a mixture of fresh hydrogen or a nonoxidizing gas and a free radical acceptor from line 103. Recycle hydrogen and free radical acceptor is introduced into the fresh feed mixture by line 106. The gas oil or the like acts as a solvent for the tar and permits easy pumping at moderate temperatures and prevents coking at hot spots in the system. The free-radical acceptor or modifier is selected from the same group as described in connection with FIG. 1. The mixture is passed by line 104 into the bottom of the first stage depolymerizer or visbreaker 105 where the mixture is maintained at a temperature of 700–900° F. (preferably 750–770° F.) and under sufficient pressure to maintain it in the liquid phase, e.g. 50–1000 p.s.i.g. The residence time of the modifier or free-radical acceptor added through lines 103 and 106 is directly proportional to its concentration in the feed. For this reason the modifier is added in amounts of 1 to 25 wt. percent based on residua feed. As described in connection with FIG. 1, a mild alkali may be slurried with the feed in the same manner and amounts as there described.

The mixture leaving depolymerizer 105 through line 108 is passed to separator 109 from which hydrogen and uncondensed gas are passed by line 110 to condensor 120 and thence by line 133 to gas separator 121 from which recycle hydrogen and hydrocarbon modifiers are recycled by lines 126 and 106. Liquid material from separator 109 is passed by line 111 to flash chamber 112 from which products boiling below about 650° F. including the modifier are removed by line 113 and passed to fractionator 130. A portion of the product from flash chamber 112 which boils below about 650° F. is withdrawn to storage by line 132. The separation in flash chamber 112 is not sharp but is only a rough approximation so that some high-boiling material is actually taken overhead through lines 113 and 132.

Products boiling approximately above 650° F. are withdrawn from flash chamber 112 by line 114 and a portion thereof is passed through filter 115 where coke and/or other solid contaminants are removed. The location of the filter is not considered critical since it may be located in line 111 leading to flash chamber 112 or it may be in line 108 so that the solids are removed immediately upon removal from the depolymerization zones 105 and 117.

The high boiling products passed through filter 115 are taken by line 116 to second stage depolymerizer 117 where they are maintained under more severe conditions than

in depolymerizer 105. Reacted products from depolymerizer 117 are removed through line 135 and combined with products from depolymerizer 105 flowing in line 108 on way to separator 109.

The remainder of the products from flash chamber 112 flowing in line 114 are taken by line 137 and recycled to depolymerizer 105 by line 102. The amount of 650° F.+ product thus diverted to depolymerizer 105 is such that the liquid feed to depolymerizer 105 contains 35 to 45% (preferably 39–41%) recycle product and with the effluent containing 45–50% (preferably 46–47%) corresponds to conversion of 25–40% of 650° F.+ in depolymerizer 105. This method of operation results in balanced conditions in the combined depolymerization zones 105 and 117. Thus, it is not necessary to force balanced conditions in a single stage and in the case of multiple stages a portion of the 650° F.+ product from filter 115 is passed by line 116 to depolymerization zone 117.

Returning now to fractionator 130, a fraction boiling below 400° F. is removed through line 122 as product. A second fraction boiling 400–650° F. or even up to 1000° F. is removed by line 123 also as product. A portion of each of these fraction is recycled by lines 127, 135, 118, and 102 back to depolymerization zone 105. Another portion, if balanced conditions are maintained, is passed by lines 127, 135, and 134 to filter 115 thence through line 116 to depolymerizer 117 wherein conditions of greater severity, e.g. temperatures between 750 and 950° F. (preferably 775–800° F.) are maintained. However the same conditions may be maintained in both depolymerizers 105 and 117, in which case the residence time is longer in depolymerizer 117 than in depolymerizer 105.

Fresh hydrogen may be added to depolymerizer 117 and line 125. Recycle hydrogen and light hydrocarbon and light hydrocarbon free radical modifiers are removed from condenser 121 by line 126 and passed to depolymerizer 105 by line 106 and depolymerizer 117 by line 136.

It is important to remember that the amount of products boiling below 650° F. or below 1000° F., as the case may be, recycled to depolymerizers 105 and 117 is critical, and must be between 20 and 50% of the total composition regardless of the distribution of the other materials. This control is made possible by withdrawing an amount of 650° F.— or 1000° F.— material from the system by lines 132, 122 and 123 necessary to maintain the proper recycle ratio. The product drawn off through lines 132, 122, and 123 is suitable as solvent for use in the chemical industry or may be further fractionated to separate out desired solvent and aromatic fractions and if desired with recycle of the high boiling material.

The multistage depolymerization differs from single stage operation in the processing of the high-boiling material. In the latter the recycle of the high boiling material is controlled so that the amount of this material fed to the depolymerizer based on total feed will be substantially the same as the amount of this high-boiling material found in the product, based on tar blend. Generally this is between 45 and 50%, preferably 46–47%.

In accordance with the embodiment of the present invention utilizing a multistage system, the conversion of the high-boiling material is conducted under mild conditions with only a minimum of coke make in the initial stage. Thus in order to keep the system in balance with no build up of high-boiling material, a portion of the high-boiling material is depolymerized under conditions of greater severity which inherently results in greater coke plus gas make, but since only a part of the material is processed, the overall coke plus gas make is less than in a single stage system which must be kept in composition balance for maximum production of low-boiling fractions.

The following examples are included to illustrate the effectiveness of the instant process for the depolymerization of hydrocarbon residua, without however, limiting the same.

EXAMPLE 1

A steam cracked tar consisting of 35.7% material boiling 430–650° F., 34.3% boiling 650–1000° F., and 30% boiling 1000° F.+ was subjected to several cycles of hydrodepolymerization for four hours each at 765° F. under 1000 p.s.i.g. hydrogen pressure while about 10% n-heptane, based on tar was thoroughly agitated with the liquid. The first cycle was carried out with no recycle and the remainder with varying amounts of recycle of the 650° F.— and 650° F.+ fractions. The following data were obtained:

Cycle.....	1	2	3	4	5	6	7
Grans tar feed.....	505	438	520	554	415.5	343.4	455.5
Feed composition, wt. percent:							
Fresh tar.....	100	40.1	40.9	35.7	39.1	32.8	36.1
430–650° F. recycle.....	0	20.6	19.7	18.1	20.7	34.0	18.0
650° F. plus recycle.....	0	39.3	39.4	46.2	40.2	33.2	45.9
Total 430–650° F. content.....	35.7	34.7	34.2	30.8	34.5	45.6	30.7
650° F. plus content.....	64.3	65.3	65.8	69.2	65.5	54.4	69.2
Product yields, based on tar:							
Wt. percent 650° F. plus.....	40.6	47.2	46.6	47	46.5	39.3	45.8
Wt. percent coke plus gas ¹	0	2.9	2.5	4.7	0.8	3.2	4.2

¹ Corrected by amount of n-heptane lost.

² 430–650° F. recycle from previous cycles. Recycles material in cycles 2 and 3 from similar operation but with catalyst.

³ 221–650° F. recycle.

The above data show that in cycles 2 and 3 the approximate composition of 40% fresh tar, 20% 430–650° F. and 40% 650° F.+ recycle is not optimum because the product contains 46–47% 650° F.+ material whereas for balanced conditions the product should contain about 39.5% and 39.1%, respectively, of the 650° F.+ material. For the system to be in balance the 650° F.+ content of the product should be about the same or less than the 650° F.+ recycle portion of the feed. The constancy of this 46–47% 650° F.+ in all operations where the total 650° F.+ content of the charge to the depolymerizer (including recycle) was equal to or greater than that of the feed is indicative that the reaction is equilibrium limited. Thus balanced conditions can be achieved by adjusting the concentrations of the 650° F.+ recycle portion of the feed to the 46–47% level. The balanced recycle condition is demonstrated in runs 4 and 7 by the lack of build up of 650° F.+ product. These runs also show that at the same time the recycle portion of the 650° F.— fraction has been adjusted from 34–35% as set forth in cycles 1, 2, 3, 5, and 6 to 30–31% in the balanced conditions of runs 4 and 7.

EXAMPLE 2

The experiment of Example 1 was continued for three more cycles except that no fresh tar was added and the temperature was raised to 775° F. The data are set forth below.

Cycle.....	8	1
Grams tar blend.....	470	408
Feed composition, wt. percent:		
Fresh tar.....	0.0	0.0
221–650° F. recycle.....	50.2	30.9
650° F. plus recycle.....	49.8	69.1
Total 650° F. minus content.....	50.2	30.9
Total 650° F. plus content.....	49.8	69.1
Wt. percent 650° F. plus in product.....	40	62
Wt. percent conversion 650° F. plus.....	18.2	24.8
Wt. percent coke plus gas ¹	10.5	10.1

¹ Corrected by amount of n-heptane lost.

The above data show that the use of 31% 650° F.— recycle is more effective than the higher dilution of 50%.

7 EXAMPLE 3

Two series of runs were made with the tar of Example 1 with and without addition of n-heptane. The following data were obtained:

Hydrodepolymerization of Steam-Cracked Tar, 4 Hours Residence Time, 765° F., 1,000 p.s.i.g. H₂ Pressure

Variable.....	Paraffin addition	No paraffin
Cycle.....	1	4
Approx. wt. percent n-heptane in blend.....	10	0
Wt. percent coke plus gas loss on tar blend.....	2.4	8.2 4.7 13.5

The above data show that the addition of paraffin hydrocarbons as modifiers or free-radical acceptors result in reduced coke and gas losses after an equal number of cycles.

EXAMPLE 4

The following data obtained by the techniques of Example 1 illustrate the effect of n-heptane and 2,2,4-trimethyl pentane as modifiers.

Hydrodepolymerization of Steam-cracked Tar, Single Pass Operation 4 Hours at 7° F., 500 p.s.i.g. H₂

Cycle.....	1	2
Modifier.....	(1)	(2)
Grams modifier.....	50	50
Grams tar.....	404.9	435.3
Grams coke plus gas.....	91.3	37.8
Grams modifier lost.....	27.8	36.2
Wt. percent gaseous prod. based on modifier.....	73.5	50
Typical gaseous components, wt. percent gas:		
Methane.....	45.3	23.4
i-Butane.....	1.6	43.9
n-Butane.....	7.4	0.8
i-Pentane.....	3.1	11.2
n-Pentane.....	1.9	0.0
Wt. percent C ₅ -221° F. liquid based on modifier.....	54	32.3
Typical liq. components, wt. percent:		
i-Pentane.....	0.4	0.2
n-Pentane.....	3.9	0.3
n-Hexane.....	3.6	0.4
Benzene.....	0.5	0.4

¹ n-Heptane.

² 2,2,4-trimethyl pentane.

³ Value abnormally high due to poor temperature control. Temperature probably higher than 775° F.

The above data show that with n-heptane as the modifier, the degradation products are predominantly normal, i.e. n-butane, n-hexane, whereas with iso-octane the degradation products are predominantly branched (isobutane, isopentane and unreacted feed not shown).

EXAMPLE 5

The following data obtained by the technique of Example 1 illustrate the effect of branch-chain paraffin modifiers in comparison with olefins of similar skeletal configuration.

Branched Chain Modifiers in Hydrodepolymerization of Steam-Cracked Tar, 500 p.s.i.g. H₂ at Start

Run No.....	93	94B	95
Modifier, 2,4,4-trimethyl.....	¹ Pentane	(2)	(3)
Grams modifier.....	50	50	50
Reaction temp., ° F.....	775	750	750
Hours of run.....	4	3.5	1
Grams tar.....	435.3	441.5	422.2
Grams of coke plus gas.....	37.8	34.1	25.2
Grams modifier lost.....	36.2	49.9	49.5
Wt. percent gaseous prod. based on modifier.....	50	56.6	49.2
Typical gaseous comp., wt percent of gas:			
Methane.....	23.4	14.7	8.7
i-Butane.....	43.9	45.9	51.0
n-Butane.....	0.8	1.1	2.2
i-Pentane.....	11.2	10.3	7.4
n-Pentane.....	0.0	0.0	0.0
Wt. percent C ₅ -230° F. liquid based on modifier.....	32.3	5.6	9.4
Typical C ₅ -230° F. liquid prod. wt. percent of fract.:			
2,2 dimethyl pentane.....	1.2	12.5	5.7
2,4 dimethyl pentane.....	1.1	1.0	0.9
2,2,4 trimethyl pentane.....	85.7	49.6	36.3
2,4,4 trimethyl pentane.....		2.5	10.9
2,5 dimethyl hexane.....		2.0	14.6
Bromine number.....		6	11

¹ Usual designation 2,2,4 trimethyl pentane. ² Pentene-1.

³ Pentene-2.

The above data show that saturated branch chain fragmentation products are produced by using branched chain

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olefins as modifiers. Furthermore, the degradation products are branched paraffins illustrating hydrogen transfer, alkylation, isomerization and demethanation reactions.

EXAMPLE 6

The following data recapitulated from Example 5 show the effect of residence time of the modifier on the yield of important products, particularly triptane.

Hydrodepolymerization of Steam-Cracked Tar, 500 p.s.i.g. H₂ Pressure at Start, Single Pass Operation

Run.....	93	94B	95
Modifier, 2,4,4 trimethyl.....	¹ Pentane	(2)	(3)
Reaction temperature, ° F.....	775	750	750
Hours of run.....	4	3.5	1
Wt. percent C ₅ -230° F. liquid, based on modifier.....	32.3	5.6	9.4
Typical components of C ₅ -230° F. liq. wt. percent:			
2,2 dimethyl pentane.....	1.2	12.5	5.7
2,4 trimethyl pentane.....	85.7	49.6	36.3
2,2,3 trimethyl butane (triptane).....	0.07	0.16	3.84

¹ Usual designation 2,2,4 trimethyl pentane. ² Pentene-1. ³ Pentene-2.

These data clearly show that the important product triptane can be obtained when the modifier is a branched paraffin or olefin such as iso-octane, alkylate, di-isobutylene, etc. Actually an increase in triptane content has been observed at conditions where the modifier consumption is so great that the yields are only indications of what might be achieved. The above data show that when the temperature was reduced to 750° F. and the reaction time for 3.5 hours and higher to 1, the triptane production was increased 24 fold. This underlines the importance of a short residence time.

The above description has shown that the depolymerization of tars and other residua can be carried out in the presence of reaction modifiers or free radical acceptors to provide a process in which coke and gas is minimized and gas oil and other products are maximized.

EXAMPLE 7

A steam cracked tar consisting of 35.7% material boiling 430-650° F., 34.3% boiling 650-1000° F., and 30% boiling 1000° F.+ and having slurried therewith about 0.5-10% CaO was subjected to several cycles of hydrodepolymerization for four hours each at 765° F. under 1000 p.s.i.g. hydrogen pressure while about 10% n-heptane, based on tar was thoroughly agitated with the liquid. The following data were obtained:

Hydrodepolymerization of Baton Rouge Cracked Tar, 1,000 p.s.i.g. H₂ Pressure, 765° F., 4 Hours Residence Time in Presence of CaO

Run No.....	1	2	3
Grams calcium oxide.....	0	50	10
Grams tar feed.....	400.4	450.7	468.4
Composition of tar feed:			
Wt. percent fresh tar.....	39.6	40.3	36.5
Wt. percent 430-650° F. recycle.....	20.4	18.3	16.5
Wt. percent 650° F. plus recycle.....	40.0	41.4	47.0
Grams n-heptane.....	50.1	50.0	50.0
Grams n-heptane consumed.....	20.5	14.3	13.1
Conversion 650° F. plus 650° F. minus, percent.....	25.0	28.8	28.6
Wt. percent coke plus gas loss (after correction for n-heptane cons.).....	7.4	3.7	3.3

The above data shows that calcium oxide was quite effective in reducing the coke plus gas losses. Approximately the same results were achieved with 10 grams of CaO as with 50, conditions otherwise being the same.

EXAMPLE 8

The experiment of Example 7 was repeated except that clarified oil from catalytic cracking was used as the feed. The following data were obtained:

Hydrodepolymerization of Clarified Oil n-Heptane and Lime Modifiers, 4 Hours at 775° F., 1,000 p.s.i.g. H₂ at Start

Run No.....	4	5	6
Grams feed.....	424.8	437.9	364.5
Grams n-heptane.....	50	50	0
Grams lime.....	50	10	10
Wt. percent conv. 650° F. plus.....	34	31	30
Grams n-heptane lost.....	10.7	12.2	-----
Coke plus gas losses, wt. percent clarified.....	1.6	1.0	4.5

The above data show that the results with the clarified oil are similar to those obtained with steam cracked tar as feed. Appreciable conversion, i.e. 30–34%, of the 650° F.+ material to 650° F.— products took place in a single pass operation. The concentration of lime above 2% appears to have little effect. In the absence of a hydrocarbon modifier (Run No. 6) the feed has to absorb all the losses to coke plus gas and hence ultimate yield is lower without the hydrocarbon modifier.

EXAMPLE 9

A steam cracked tar consisting of 35.7% material boiling 430–650° F., 34.3% boiling 650–1000° F., and 30% boiling 1000° F.+ was subjected to several cycles of hydrodepolymerization in two stages for four hours each at 765° F. under 1000 p.s.i.g. hydrogen pressure while about 10% n-heptane, based on tar was thoroughly agitated with the liquid. The following data were obtained:

Hydrodepolymerization of Steam Cracked Tar, 1,000 p.s.i.g. Hydrogen Pressure at Start; 4 Hours Residence Time, About 10% n-Heptane on Tar Feed Added

Operation	Balanced condition single stage	Balanced condition multiple stage
Proposed stage.....	I	II
Data from batch operation cycle.....	7	11
Temperature, ° F.....	765	775
Feed composition:		
Wt. percent fresh S-2 tar.....	36.1	39.1
Wt. percent 650° F. minus recycle.....	18.0	20.7
Wt. percent 650° F. plus recycle.....	45.9	40.2
Wt. percent 650° F. plus in product.....	45.8	46.5
Conversion 650° F. plus material, wt. percent.....	34	29
Coke plus gas losses, wt. percent.....	4.2	0.8
Coke plus gas losses, at balanced conditions, wt. percent fresh S-2 tar.....	11.5	7.5
Est. ultimate yield, vol. percent fresh tar.....	93	97

¹ Corrected by amount of n-heptane lost.

² Calculated value using part of 650° F. plus from Stage I in Stage II.

³ 48% of total 650 plus product from Stage I.

The above data show that the use of the multiple stage system results in higher yields with smaller losses to coke and gas.

The above description does not by any means cover the possible uses of this invention or the forms it may assume but serves to illustrate its fundamental principles and an assembly in which the novel features as disclosed have been incorporated. It is obvious that changes in the details may be made without departing from either its novel characteristics or the spirit and scope of the invention as defined in the appended claims. For example it is within the scope of this invention to use a multicompartmented reactor or combination of reactors instead of a series of single reactors since the term "stage" is intended to denote a condition of concentration and only to a lesser extent one of temperature and residence time. It is also within the scope of this invention to operate depolymerizer 5 of FIG. 1 or both of the depolymerizers 105 and 117 of FIG. 2 in the absence of hydrogen.

EXAMPLE 10

The foregoing data have shown that conversion of the high-boiling components in steam-cracked tar are affected by dilution and by amount of low-boiling materials added as solvent and that high dilution tends to retard the depolymerization of the high-boiling components to 650° F.—. The same analogy applies to conversion of the 1000° F.+ material. This is demonstrated by experimental data in which the accumulated 650° F.+ material from previous cycles (A) was blended with 430–650° F. solvent and depolymerized similarly to conditions in a previous example but the product was separated into 430–650° F., 650–1000° F., and 1000° F.+ product. This 1000° F.+ product was diluted with 430–650° F. product from a similar depolymerization process (Run B) and with catalytic cracking clarified oil containing predominantly 650–1000° F. material and after depolymerization was separated so

as to ascertain conversion of the 1000° F.+ product. These data are summarized as follows:

Run No.....	77	81
5 Cycle No.....	11	12
Tar feed, grams.....	383.8	480.5
Source of 430–650° F. recycle.....	Composite	Run B.
Source of 650–1,000° F. recycle, run.....	A. Clarified oil.	Run 77. ¹
Composition:		
Wt. percent fresh steam-cracked tar.....	0	0
Wt. percent 430–650° F. recycle.....	28.8	29.7
Wt. percent 650–1,000° F. recycle.....	71.7	70.3 ²
Wt. percent 1,000° F. plus recycle.....	48.8	38.1 ²
Modifier:		
Grams heptane.....	50	50
Grams CaO.....	0	50
Operating conditions:		
Temperature, ° F.....	775	775
Hours of run.....	4	4
Pressure, p.s.i.g.:		
At start.....	1,000	1,000
Maximum.....	1,740	1,650

¹ Refers to steam-cracked tar product and not to clarified oil solvent.

² 1,000° F. plus material from run 77 blended with catalytic clarified oil.

Run.....	77	81
Recoveries, grams:		
Hydrocarbon modifier.....	27.7	42.1
Liquid ex modifier, grams:		
C ₄ –221° F.....	1.1	1.8
221–375° F.....	4.2	8.6
375–430° F.....	8.6	35.1
430–650° F.....	152.4	140.9
650–1,000° F.....	35.1	120.0
1,000° F. plus.....	160.2	158.9
Gas.....	15.8	10.8
Coke.....	30.8	5.0
Overall material bal., wt. percent.....	100.5	98.7
Material bal. based on tar.....	103.8	100.1
Conversions, wt. percent:		
650° F. plus to 650° F. minus.....	29.0	20.0
1,000° F. plus to 1,000° F. minus.....	18.9	13.4

The conversion of hydrocarbon modifier as represented by low modifier recovery and increase in gas, liquid, and coke yields is typical of depolymerization reactions with hydrocarbon modifiers.

EXAMPLE 11

A feed composition similar to that used in Run 77 and consisting of about 31% fresh steam-cracked tar, 30.6% 430–1000° F. recycle and 38.4% 1000° F.+ recycle from previous operation together with about 10% hydrocarbon modifier consisting of either branched or straight chain hydrocarbons is thermally depolymerized at temperatures in the range of 750–790° F., preferably about 775° F. for residence times of 1–6 hours, preferably 2–4 hours and the products are separated into 430° F. and lighter fractions, 430–1000° F. hydrocracker feed and 100° F.+ unconverted product. The latter is recycled to extinction.

EXAMPLE 12

A feed composition, similar to that used in Run 81 consisting of about 17% fresh steam-cracked tar 49.9% 430–1000° F. recycle product and 33.1% recycle 1000° F.+ product together with up to 10% hydrocarbon modifier, and if desired with an alkaline modifier, is depolymerized at temperatures in the range of 750–790° F. preferably about 775° F. for residence times of 1–6 hours preferably 2–6 hours and the products are separated into 430° F.— fractions, 430–1000° F., and 1000° F.+ fractions. The latter is recycled to extinction. The higher dilution of Run 81, hence less fresh tar feed, has the characteristic of smaller losses to coke and gas.

EXAMPLE 13

The foregoing examples are based upon a steam-cracked tar containing 30% 1000° F.+ material. Since this value may vary over wide ranges a general illustration of the process in keeping with the data of Runs 77 and 81 is a feed having composition of

	Percent
Fresh tar feed	10–50
430–1000° F. recycle	15–50
1000° F.+ recycle	30–40

This feed is depolymerized at temperatures in the range of 750–790° F. for a period of 1–6 hours and after separation of the 1000° F.+ portion from the 1000° F.– portion the former is blended with fresh feed and 430–1000° F. diluent and recycled to extinction.

We claim:

1. A process for the thermal treatment of a hydrocarbon residuum feed having Conradson carbon numbers between 5 and 40 in a reaction zone which comprises heating said residuum under a pressure sufficient to maintain the residuum in the liquid phase and at a temperature between 700 and 900° F. in the additional presence of a free radical acceptor, chosen from the group consisting of 1–25 wt. percent of an acyclic hydrocarbon modifier, having 2 to 20 carbon atoms, 0.1 to 50 wt. percent of a mild alkali, and mixtures thereof using 0.1 to 1 part by weight of alkali per part by weight of feed where mixtures thereof are utilized, removing reacted products, and separating a portion of the reacted products into a high-boiling fraction and a low-boiling fraction, recycling said high-boiling fraction and said low-boiling fraction to the reaction zone at rate sufficient to maintain a balanced condition wherein these fractions are at about the same level of concentration as these fractions are present in the residuum feed introduced to the reaction zone, these components constituting between 20 and 50% of the total feed composition.

2. The process according to claim 1 in which the balanced condition is achieved with a recycle rate of the high-boiling fraction of 46–47%.

3. The process of claim 1 in which the free-radical acceptor is CaO.

4. The process of claim 1 in which the residence time of the acyclic hydrocarbon modifier within the reaction zone is one hour or less and that of the residua-recycle mixture is 1 to 6 hours.

5. The process of claim 4 in which the modifier is n-heptane.

6. The process of claim 4 in which the modifier is 2,2,4-trimethyl pentane.

7. The process of claim 4 in which the modifier is 2,4,4-trimethyl pentene-1.

8. The process of claim 4 in which the process is carried out at 750° F. and the residence time of the 2,4,4-trimethyl pentene and olefins of similar skeletal configuration is 1 hour whereby the yield of triptane is enhanced.

9. The process of claim 4 in which the modifier is 2,4,4-trimethyl pentene-2.

10. The process of claim 4 in which the modifier is a light virgin C₅–C₇ naphtha.

11. The process of claim 1 in which the low-boiling fraction boils below 650–1000° F. and the high-boiling fraction boils above 650–1000° F.

12. The process of claim 1 in which the low-boiling fraction boils below 650° F. and the high-boiling fraction boils above 650° F.

13. The process of claim 1 in which the low-boiling fraction boils below 1000° F. and the high-boiling fraction boils above 1000° F.

14. A process for the thermal treatment of hydrocarbon residuum having Conradson carbon numbers between 5 and 40 which comprises heating said residuum in a first reaction zone under a pressure sufficient to maintain the residuum in the liquid phase and at a temperature between 700 and 900° F. in the additional presence of

1 to 25 wt. percent of an acyclic hydrocarbon modifier, having 2 to 20 carbon atoms, removing reacted residuum from said first reaction zone, and passing a portion of it together with an acyclic hydrocarbon modifier to a second reaction zone under more severe conditions than in said first reaction zone under a pressure sufficient to maintain the residuum in the liquid phase, combining the reaction products from both reaction zones, separating the reaction products into a high-boiling fraction and a low-boiling fraction, recycling the low-boiling fraction to each of said reaction zones such that the feed to the two reaction zones contains 20 to 50% of low-boiling material exclusive of the modifier and recycling an amount of the high-boiling fraction from the two reaction zones so that the high-boiling recycle from the combined reaction zones is equal to the recycle portion in the feed to the first zone.

15. The process of claim 14 in which the low-boiling fraction boils below 650–1000° F. and the high-boiling fraction boils above 650–1000° F.

16. The process of claim 14 in which the low-boiling fraction boils below 650° F. and the high-boiling fraction boils above 650° F.

17. The process of claim 14 in which the low-boiling fraction boils below 1000° F. and the high-boiling fraction boils above 1000° F.

18. The process of claim 14 in which a conversion of 25–40% is maintained in the first reaction zone and 25–30% in the second reaction zone.

19. The process of claim 14 in which the first reaction zone is maintained at 700–900° F. and the second reaction zone at 750–950° F.

20. The process of claim 14 in which the first reaction zone is maintained at 750–770° F. and the second reaction zone at 775–800° F.

21. The process of claim 19 in which the residence time of the acyclic hydrocarbon modifier is longer in the second reaction zone than in the first.

22. The process of claim 19 in which the modifier is n-heptane.

23. The process of claim 19 in which the modifier is n-pentane.

24. The process of claim 19 in which the modifier is 2,2,4-trimethyl pentane.

25. The process of claim 19 in which the modifier is 2,4,4-trimethyl pentene-1.

26. The process of claim 19 in which the modifier is 2,4,4-trimethyl pentene-2.

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